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EVALUATION OF ADHESIVE FORCES AND THE SPECIFIC SURFACE ENERGY OF ZIRCONIA STABILIZED BY YTTRIA WITH ALUMINA ADDITIONS CERAMIC BY AFM METHOD

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Abstract. The adhesive forces and the specific surface energy of ceramic material surfaces are very important for further tribological and biomedical applications of ceramics. Partially stabilized zirconia (zirconium oxide) is popular for manufacturing various medical products. ZrO_2 stabilized by Y_2O_3 with additions of 5 wt% alumina was produced by slip casting method with a subsequent sintering. Structure and chemical composition of ceramic surface were analysed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. The adhesive forces were measured by means of atomic force microscopy (AFM) method. Parameters of specific surface energy show some range of values. Results demonstrate the importance of evaluation not only total surface specific energy but its local parameters in the points of additives concentration on the surface of material.
Keywords: ceramics; composites; AFM; adhesive forces; specific surface energy.

Introduction. The material surface properties play the important role in the main processes on biomedical material interfaces [1].

The adhesive forces and the specific surface energy of ceramic products are essential in the processes of products manufacturing, as well as in the operation of the finished surfaces for tribological and biomedical applications. Since it is not possible to measure directly the surface free energy of a solid, its determination is achieved, at present, by many indirect methods. Among other, the methods based on the contact angle measurements for appropriately chosen systems are the most popular [2–4].

Partially stabilized zirconia (zirconium oxide) is used to manufacture various medical products due to its good biocompatibility, high strength, high compression resistance and resistance to crack propagation [5]. In references have been shown that the specific surface energy of zirconia can make superiority for some processes on the surface of ceramic, for example, in reducing bacterial adhesion [6, 7].

One of the main problems of the evaluation of the solid surface free energy is to express the interfacial solid-liquid free energy in the Young×s Equation as a function of the surface free energy of the solid and of the liquid involved. The influence of different additives such as MgO, Y_2O_3, Al_2O_3 on the surface free energy of ZrO_2 ceramic was analyzed on the base of tensiometric measurements [8, 9].

Often, there are no alternatives to probe technique in atomic force spectroscopy regime in the case of direct experimental measurements of the adhesion forces between the different phases of the material with a size of several hundred nanometers. Depending on the materials type, special probes are designed with tips made from investigated or coated materials for adhesion measurements [10–14]. However, in the case of problem to estimate not only adhesive forces of a whole surface but also the adhesion forces of the different phases, probes with standard silicon tips are more preferred due to possibility to provide the required localization. The aim of this study was to evaluate the values of the adhesion forces and the specific surface energy between the different phases on the surface of the ceramic sample of zirconia stabilized by 3 wt % ittria with additions of 5 wt% alumina.

Materials and Methods. Zirconia ZrO_2 (3% Y_2O_3) (Stanford Materials Corporation, USA), with a size of particles of 0.05 μm and alumina Al_2O_3 (Almatis, Germany) with a size of particles of 0.5 μm were used as initial materials. ZrO_2 – 3% Y_2O_3 ceramic was produced by slip casting method with a subsequent sintering. Slips were prepared from the powders by adding distilled water and deflocculating agent. As a deflocculating agent DOLAPIX grade FF 7 (Germany) was used. The sample of ZrO_2 stabilized by Y_2O_3 with additions of 5 wt% alumina was produced from the slips, using casting into plaster moulds. The sample were sintered at a temperature of T = 1600 °C with the rate of heating and cooling about 200 C/h using a laboratory furnace Nabertherm P310 (Germany) equipped with molybdenum disilicide heaters. The method allows to produce dense finely crystalline structure of zirconia with uniformly arranged disperse particles of alumina.

The structure and the chemical composition of the surface were analysed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy using a model Mira Tescan (Oxford). The adhesive forces were measured by means of atomic force microscopy (AFM) method NT-206 (Belarus). For a reliable determination of adhesion forces, when the stiffness of the console allows to feel not only adhesive forces but also cut off the probe from the surface, probes are used with a V-shaped console type NSC 11 with a hardness of 3.0 N/m («Mikromash», Estonia). The adhesion force F_a between the silicon tip and the surface of investigated material is defined as the maximum deflection (*Defl*) of the console in the separation of the tip from the surface multiplied by the stiffness of the console k: $F_a = k \cdot Defl$.

The specific surface energy (the work of adhesion) was determined according to the theory Deryagin-Muller-Toporov (DMT) for the contact of hard materials by the formula (1) [14]:

$$\gamma = F_a/(2\pi R), \quad (1)$$

where F_a – the adhesion interaction force between the probe tip and the sample surface, N; R – probe tip radius, m. The measurements were made on air.

The work of adhesion is calculated equal to the specific energy per unit of the contact area required to break the contact tip and the surface under study. To determine the actual area of the contact patch, a TGT-type calibration grating for tip characterization was scanned by the probe (Fig. 1).

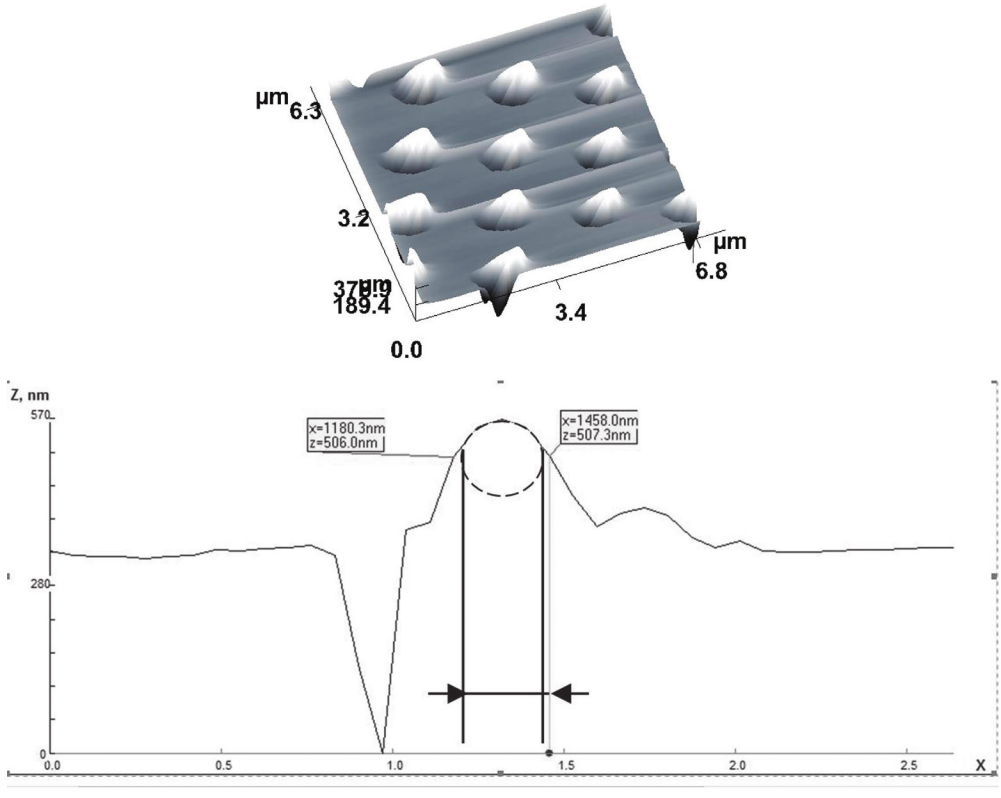


Fig. 1. AFM images of TGT calibration grating for tip characterization: *a* – topography regime; *b* – profile through a single element of the test

Results and Discussion. The surface topography and morphology of ZrO_2 stabilized by Y_2O_3 ceramic with 5 wt% Al_2O_3 were investigated by electron scanning microscope. Fig. 2 demonstrates the surface microstructure of the sample after sintering at temperature 1600 ºC, which has a very dense granular structure. Such structure formation was typical for 5% additions of alumina in zirconia-based ceramic stabilized by yttria.

The chemical composition of ZrO_2 stabilized by Y_2O_3 ceramic with additives of Al_2O_3 were investigated by energy dispersive X-ray (EDX) spectroscopy method. The map of the distribution of chemical elements on the surface of the ceramic has shown its homogeneity within the diameter of the exciting electron beam (fig. 3). Only some regions enriched by aluminum have been detected

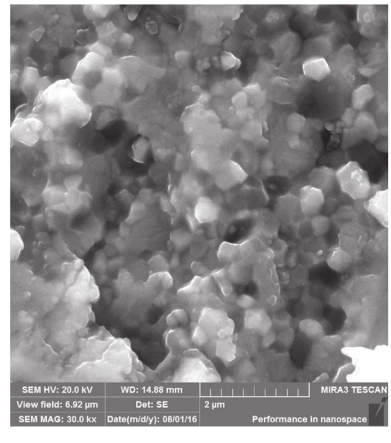
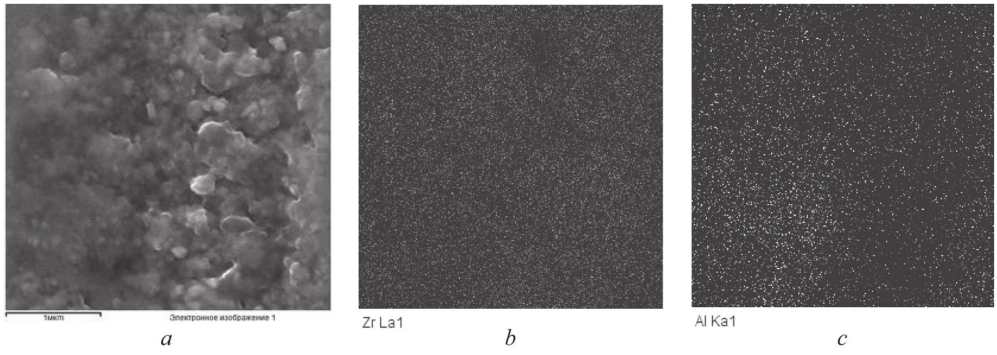


Fig. 2. Surface microstructure of sample ZrO_2 stabilized by Y_2O_3 ceramic with 5 wt% Al_2O_3 by SEM, ×30000



a *b* *c*

Fig. 3. The map of Zr and Al distribution on the ceramic surface: *a* – microstructure of area; *b* – the map of Zr distribution with its uniformly distribution; *c* – the map of Al distribution with its enriched in the left side

on the map of elements distribution (fig. 3 *c*). The EDX spectra were observed and confirmed the presence of content of 5% Al_2O_3 in the sample ZrO_2 (3% Y_2O_3). The difference in the element content was determined only with analysis in point (Tab. 1). In fig.4 the points of analysis are shown. The area of ceramic is the same as in fig.2, but fig. 4 shows the sample ZrO_2 stabilized by Y_2O_3 ceramic with 5 wt% Al_2O_3 using backscattered electrons detector (BSE). The contrast image in BSE regime is created by the averaging of atomic numbers of phases in comparison to their secondary electrons (SE) contrast (fig. 2) due to the relief. Since heavier elements (Zr, Y, Hf) backscatter electrons more strongly than lighter elements (Al), and therefore phases containing Zr appear brighter in the image and phases containing Al appear darker, BSE helps detect areas enriched Al. The point which are enriched with Al are shown in Tab.1 with green colour. So despite the crystalline inclusions of alumina are uniformly distributed over the volume of the sample, the difference in the chemical composition and in properties exists in local scale.

Table 1. **The chemical composition by EDX spectra of the sample ZrO_2 stabilized by Y_2O_3 ceramic with 5 wt% Al_2O_3 according to SEM images Fig. 4** *a*

Spectra	Al	Y	Zr	Hf	O
point 1	1.4	2.7	68.0	1.8	26.2
point 2	13.1	1.8	53.6	0.5	31.0
point 3	3.1	2.3	66.1	1.7	26.8
point 4	1.4	2.3	69.0	1.1	26.2
point 5	7.0	2.3	60.8	1.5	28.4
point 6	15.2	1.7	49.9	1.5	31.8
point 7	7.8	1.9	60.3	1.1	28.8
point 8	18.5	1.5	45.8	1.2	33.1

These areas were wider extended over the surface of the section (fig. 3, *a*) due to the plasticity and the alumina content was higher than the total content in the material (fig. 3, *c*). The sections consist of the areas with very apparent grains of different phases and a smooth surface, where all phases are smeared over plastic component (fig. 3, *c*). The composition of such zones was enriched by aluminum (up to 18 wt% compared with normal 3 wt%) and depleted by zirconium (45–53 wt% compared with normal 60–69 wt%). The probability of AFM detecting into this zone is negligible. The single grains, enriched with zirconium and plastic mixed layer, comprising zirconium and aluminum are the main surfaces of the AFM study of the ceramic.

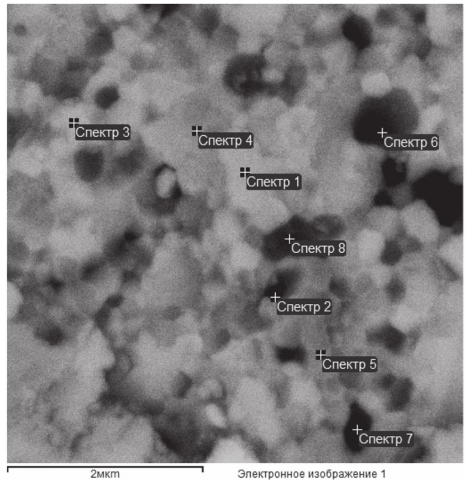
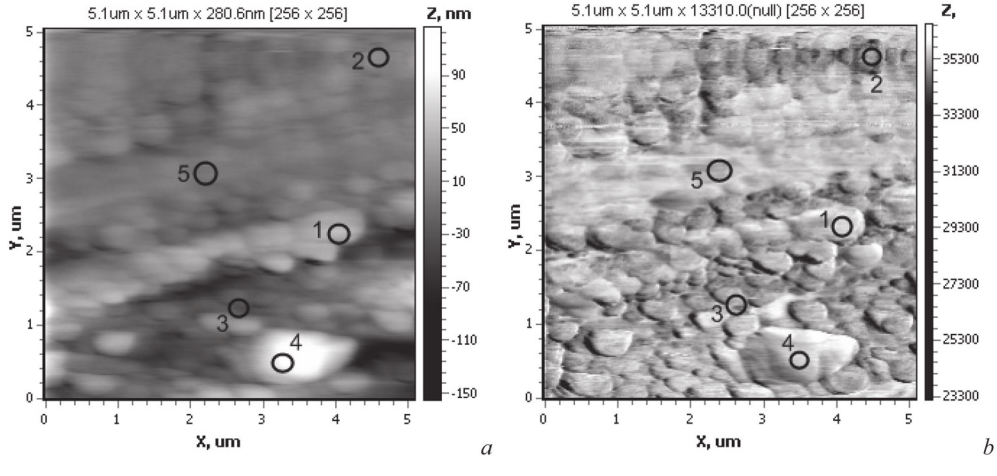


Fig. 4. Surface microstructure of sample ZrO_2 stabilized by Y_2O_3 ceramic with 5 wt% Al_2O_3 by SEM with BSE detector

The adhesive forces were measured by means of AFM method. Fig. 5 demonstrates the AFM images of the surface of ZrO_2 stabilized by Y_2O_3 with 5 wt% Al_2O_3 ceramic with points for adhesive forces evaluation. Fig. 5, *b* obtained in the AFM regime «Torsion» which is more sensitive to different phases and surface layers due to torsion twist of the cantilever under the interacting surface and the probe tip. Among the structural elements of the surface we can choose points which are grains enriched Zr (points 1 and 4) and points which belong to plastically changed surface

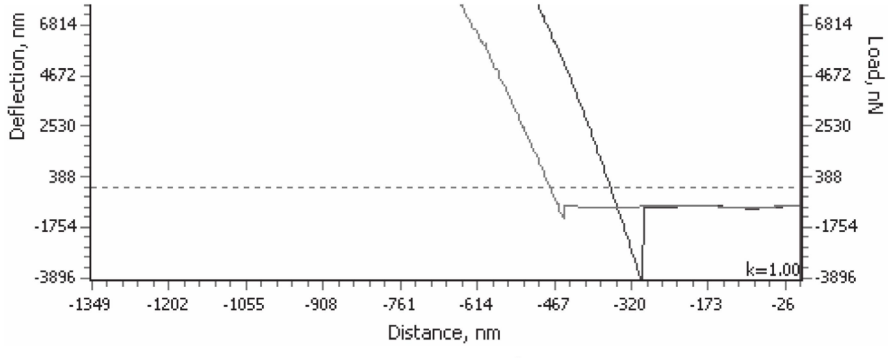


a *b*

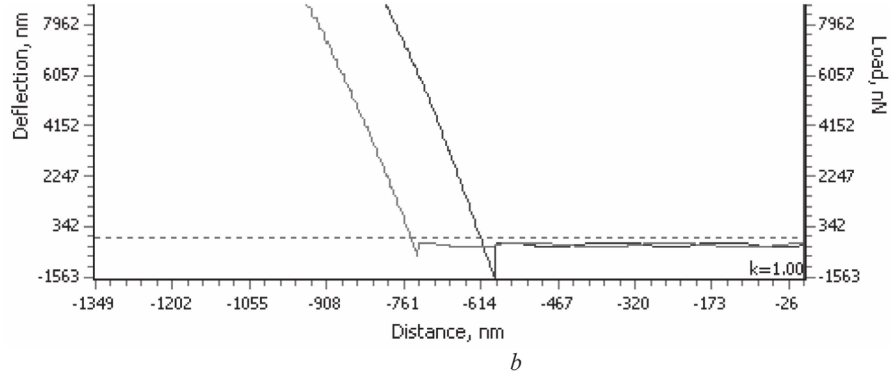
Fig. 5. AFM images of the surface of ZrO_2 stabilized by Y_2O_3 with 5 wt% Al_2O_3 ceramic with points for adhesive forces evaluation: *a* – topography regime; *b* – lateral force regime «Torsion»; points 1 and 4 – obviously from grains enriched Zr; point 5 – from surface layer enriched Al

layer enriched Al (point 5). The specific surface energy (the work of adhesion) was measured by curves of «direct contact - pull off» the probe from the different areas of the surface (Fig. 6, *a*, *b*).Values of the adhesive forces and the specific surface energy in the different points of the ceramic surface are measured by AFM method and presented in Tab. 2. So we can see a significant difference in the adhesion force value between points 4 and 5.

The modification of surface properties by adding different additives into the zirconia ceramic matrix leads to principal changing of specific surface energy parameters (Tab. 3). Exactly the adding of alumina leads to decrease of surface energy in ceramic based on ZrO_2. Some excess (overestimation) of the adhesion forces and surface energy absolute values can be explained by the experimental environment. Usually, these investigations are performed in a controlled environment or atmosphere [15]. Thus the specific surface energy between silicon and mica, measured in [16] using AFM amounted to 110 mJ/ m^2 in water, while in air 215 mJ/m^2 [16]. The values excess can be explained in air by the presence of fluid microquantity on the surfaces and the existence of the capillary effect. On the other hand, even in these simple experimental environment, a distinction between specific surface energy values of different phases in the solid material is possible.



a



b

Fig. 6. Experimental results for evaluation of adhesive force by curves of «direct contact - pull off» the probe from the different points of the ceramic surface: *a* – curves from grain enriched Zr; *b* – curves from surface layer enriched Al

Table 2. **Adhesive force and specific surface energy in the different points of ceramic surface according to Fig. 4, b by AFM method**

Area	Point	Deflection of cantilever, nm	Adhesion force, nN	Specific surface energy, mJ/m^2	Mechanical stress for contact break, MPa
1	1	60,1	180	239	3.98
	2	55,8	167	222	3.07
	3	29,0	87	115	1.92
	4	68,7	206	273	4.56
	5	18,6	56	74	1.23
2	1	15,7	47	63	1.04
	2	38,1	114	151	2.52

This phenomenon was previously detected and analyzed by means of tensiometric measurements [8, 9]. Furthermore, different types of additives result in increase of contact angles and decrease of surface free energy. The parameters of specific surface energy measured by AFM method demonstrate some range of values in the points of different phase's concentration. The results of present study demonstrate the importance of evaluation not only total surface free energy but its local parameters in the points of additives concentration on the surface of material.

Conclusions. The results show that the surface properties of ZrO_2 stabilized by 3 wt% Y_2O_3 with 5 wt% Al_2O_3 ceramic are strongly influenced by phase and element composition of ceramics. The properties depend on surface microstructure with crystalline inclusions of alumina uniformly distributed over the volume of the zirconia ceramic. The EDX spectra were detected the presence of content of 5% Al_2O_3 in the ZrO_2 (3% Y_2O_3) matrix. The composition of some zones was enriched by aluminum (up to 18 wt% compared with normal 3 wt%) and depleted by zirconium (45–53 wt% compared with normal 60–69 wt%) according to SEM/EDX results. The increase of alumina additives concentration on the surface leads to decrease of the specific surface energy. Generally, the obtained results demonstrate that a combination of ceramic manufacturing and treatment conditions with optimized surface chemistry allows to tailor specific surface energy parameters.

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